

AN ABSTRACT OF THE THESIS OF

Joseph M. Ninosky for the degree of Master of Science in Chemical Engineering
presented on August 26, 1998. Title: Reaction Kinetics and Mass Transport in the
Electroless Deposition of Copper.

Abstract approved:
Redacted for privacy

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Electroless copper deposition is employed extensively in the printed circuit board industry, yet the current approach to the implementation of this process is largely a trial and error type method. To allow for optimization of this technology, a better fundamental understanding of the process is required. Issues and concerns germane to the electroless deposition of copper are discussed with a fundamental chemical engineering analysis of the electroless copper plating bath. A rotating copper disk is used as the substrate so that an analytical solution for the mass transfer to the surface can be obtained.

Three plating rate regimes are found to exist in this study: an initial regime which is mass transfer limited, a steady regime which is surface reaction limited, and a nucleation regime where growth is believed to be limited by the number of available sites. The plating rate is found to be independent of the EDTA concentration above an atomic ratio of EDTA to CuSO_4 of 2:1. The inherent kinetics of the electroless copper deposition reaction are quantified in terms of the rate law which is expressed as a function of the cupric ion interfacial concentration, the bulk concentrations of hydroxide

and formaldehyde, a reaction rate constant, and the reaction order with respect to cupric ion concentration. The reaction rate for the steady regime with copper as the limiting reagent and the formaldehyde and sodium hydroxide concentrations held at 0.50 M and 0.30 M, respectively, is found to be: $R = (17.28 \pm 0.41)[\text{Cu(EDTA)}^{2-}]_s^{0.40 \pm 0.01} \mu\text{m/hr.}$

The plating rates obtained using the non-catalyzed copper substrate are found to be 5-10 times slower when compared with those in the literature which do employ a catalyzed substrate. Finally, the model obtained is used to predict deposition rates under different experimental conditions. In all cases investigated, the agreement between model prediction and the actual measured deposition rate is within 13%.

REACTION KINETICS AND MASS TRANSPORT IN THE ELECTROLESS
DEPOSITION OF COPPER

by

Joseph M. Ninosky

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Presented August 26, 1998
Commencement June 1999

Master of Science thesis of Joseph M. Ninosky presented on August 26, 1998

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Joseph M. Ninosky, Author

ACKNOWLEDGEMENT

First and foremost, I must thank my mother, Nancy Ninosky, and my father, John Ninosky, for their undying and complete support of my efforts throughout my life. I could not imagine a better pair to ultimately rely upon. I will never be able to completely describe in words the love and gratitude I feel towards them. I thank you both for everything.

To my brother, Matt Ninosky, my best friend, my closest ally, and at times my greatest inspiration. I thank you for the friendship that allowed me to suck it up when things seemed overwhelming. You were always there, and I can only hope that you always will be.

To Nick Wannenmacher, you not only taught me valuable lessons about the real world, but provided a superior example of patience and understanding. Without your support this entire endeavor would have been impossible. I can think of no better example for an aspiring engineer. Thank you very much.

I would like to thank Skip Rochefort for providing me an opportunity to attend Oregon State University, and my major professor, Milo Koretsky, for the guidance and supervision which enabled me to grow as an engineer. I definitely learned a lot.

Finally, I would like to thank several people who over the years believed in the American Psycho: Eric Nelson, Jason Smith, Laura Johnston, Jim Junkin, Mike Skocilich, Alfredo Zepeda, Mike Penjoyan, Pat O'Neil, Pao Chau, Tracy Gray. Your friendship meant more to me than you will ever know.

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REACTION KINETICS AND MASS TRANSPORT IN THE ELECTROLESS DEPOSITION OF COPPER

I. INTRODUCTION

The electroless deposition of copper is a process which is used extensively in the fabrication of printed circuit boards. The deposition is used to plate dielectric through holes with a conductive layer of copper that may then serve as a substrate for subsequent electrolytic growth. The plating baths used are primarily composed of four major constituents: cupric ions, formaldehyde, sodium hydroxide, and a chelating agent. The cupric ions are reduced to the metallic state by the formaldehyde in a caustic aqueous medium, with the chelating agent serving as a complexing agent which prevents the cupric ions from being reduced in solution rather than upon the desired substrate.

The bulk of the work done in examining the kinetics of the electroless deposition of copper focuses on conditions that mimic those employed by industry. As such, much of the published efforts are empirical in nature and fail to address the basic physics of the process. Rather, the entire plating procedure is treated as a black box which can be described by an apparent rate law which depends upon the bulk concentrations of the bath constituents (formaldehyde, hydroxide ion, cupric ions, and chelating agent), the bath temperature, and a reaction rate constant. This approach fails to separate the transport rates from the inherent reaction rates.

One such article examines the plating rates of several baths and ascribes an empirical rate law to the process [Donahue, 1980b]. The experiments are performed in a

non-agitated bath and the orders of reaction for each reagent are compared to other values reported in the literature. The discrepancies between the reaction orders are attributed to mass transport effects and to differing catalytic surface properties. A significant result of the published reaction orders is that the chelating ligand order is almost always found to be near zero.

Mass transport effects are examined by Donahue [Donahue, 1980a]. The work focuses on the determination of the interfacial concentrations of the reactant species as a function of bulk concentrations, diffusivities, and reaction stoichiometry. The author compares the reaction orders for cupric ion reported by previous authors and comes to the conclusion that the reaction mechanism for the cupric ions is most likely independent of the chelating ligand employed. The author also concludes that the mass transport of reactant species in a standard non-agitated copper plating bath is dominated by the gas bubble formation due to hydrogen evolution during the plating reaction, and that plating baths with a bulk cupric ion concentration less than 0.2 M will fall into a mass transport limiting regime. However, the author points out that in the presence of forced convection, the gas bubble formation does not contribute significantly to the mass transfer control.

As the mass transport of the cupric ions to the board surface play a major role in the plating rate, Ying et. al. examine the density and viscosity of electroless baths as a function of constituent concentrations and temperature [Ying, 1988]. These properties of the electroless bath will affect the flow patterns of the bath when subjected to agitation. The diffusion coefficients for the cupric ion-EDTA complex and the cupric ion-Quadrol complex are determined as functions of the bath temperature and kinematic viscosity.

Dumesic et. al. use a rotating cylinder to quantify the mass transfer of the cupric ions to the surface of a catalyzed glass substrate [Dumesic, 1974]. It is found that two separate regimes of growth exist, an initial fast surface coverage of the substrate, and a slower subsequent plating of the cupric ions upon the electroless copper surface. The experiments are limited to plating times of less than ten minutes due to the experimental procedure employed. The reaction order with respect to the cupric ion concentration is found to be 0.37, but no rate law is proposed.

The previous work focuses almost entirely upon the electroless plating of copper using a catalyzed surface, predominately a palladium activated substrate. The activity of a palladium activated copper substrate is reported to be an order of magnitude greater than that of a non-activated copper surface [El-Raghy, 1979]. It was suspected that the transport of the catalyst from the deposit-substrate to the deposit-solution interface during the electroless plating process contributed to this phenomenon, but this theory was disproved [Gottesfeld, 1986].

An alternative approach to those discussed above is to use electrochemical techniques to investigate the role of the electrolyte composition upon the mechanism of the electroless copper deposition process [Mishra, 1996]. The authors monitor the mixed potential of the plating process under differing bath conditions as the plating occurs. They also use a two cell geometry to isolate anodic and cathodic processes. From the resulting polarization plots, it is determined that as the cupric ions are depleted from solution, the process changes from anodic to cathodic control. In addition to the complexity of these measurements, there is some discrepancy in the data obtained. Potentiostatic, galvanostatic, and pseudo steady-state scans show the same general trends,

but different results. Moreover, while mass transfer effects are noticed under certain reaction conditions, no effort is made to control mass transfer by varying the cell geometry.

In this study, a more heuristic approach is taken. In order to determine the inherent, rather than the apparent, reaction rate for the electroless deposition of copper, a rotating copper disk serves as the surface for copper deposition. The rotating disk geometry allows an exact analytical solution of the fluid flow in the system. Thus the experiments can be performed in an environment where the mass transfer effects may be varied and quantitatively accounted for, leading to a determination of the surface concentration of the reactants. The chelating ligand is accounted for in the diffusion coefficient of the copper ion-EDTA complex used to determine the mass transport of the cupric ions to the disk surface. The cupric ions are kept as the limiting reagent, which corresponds to actual industrial bath conditions due to cost. If the hydroxide and formaldehyde bulk concentrations are kept in stoichiometric excess, the reaction rate may be represented as a function of the bulk hydroxide and formaldehyde concentrations, the interfacial concentration of the cupric ion complex, a reaction rate constant, and the order with respect to the cupric ion concentration. It is the aim of this approach to provide a simple chemical engineering analysis to the electroless plating process such that the rate may be predicted for a typical industrial type bath.

II. EXPERIMENTAL

II.1. Apparatus

A schematic of the experimental set up is shown in Figure 1. Photographs of the apparatus are shown in Figures 2a and 2b. The reactor consists of a rotating disk substrate which is immersed in plating solution. The rotation speed is varied between 0 to 200 RPM. The reactor consists of a 2 liter Pyrex beaker with 1 liter of plating solution. Table 1 lists the base case composition for the four chemical constituents of the plating solution:

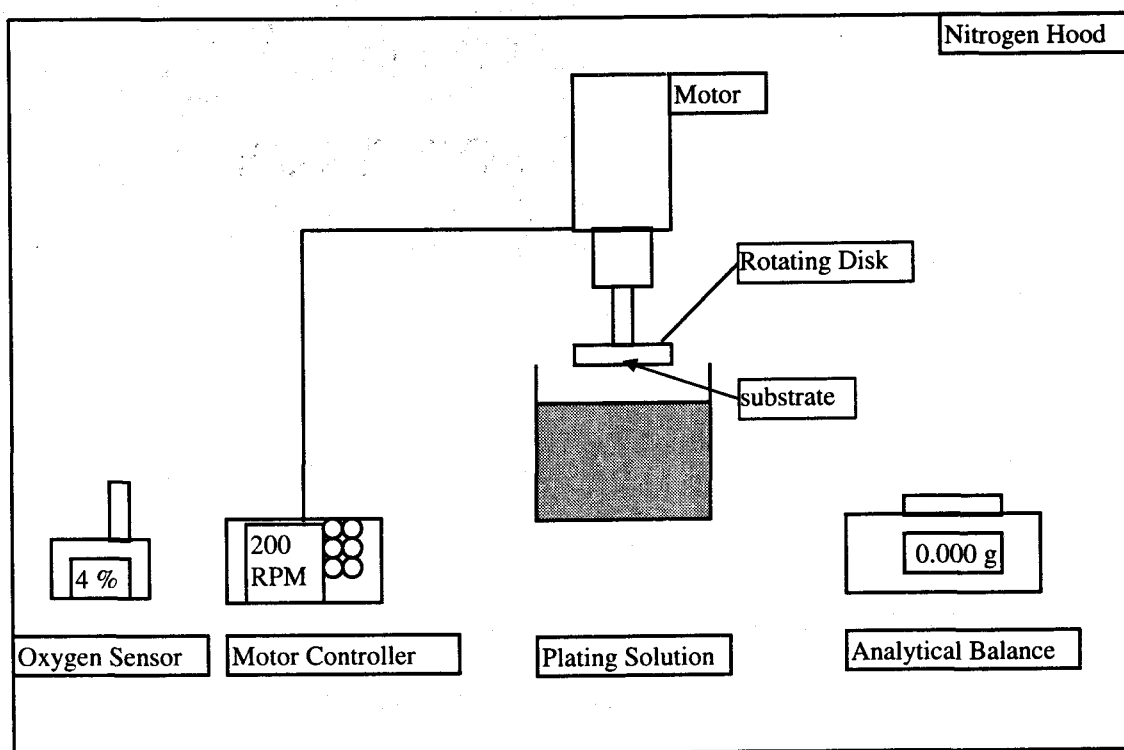


Figure 1. Experimental setup for kinetic studies of the electroless deposition of copper.

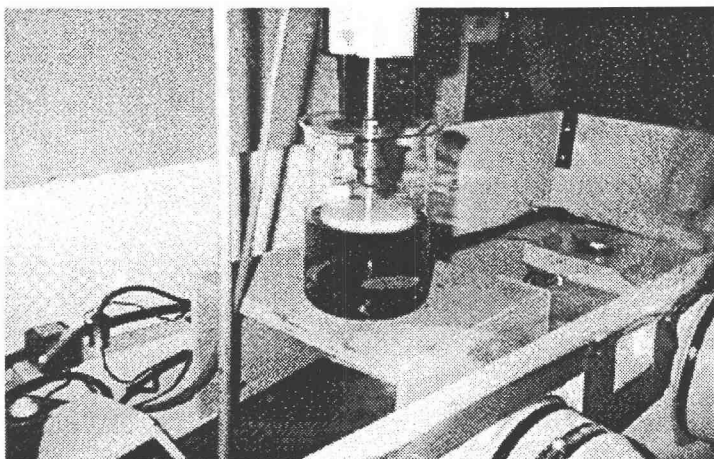


Figure 2a. Rotating disk reactor for electroless copper deposition.

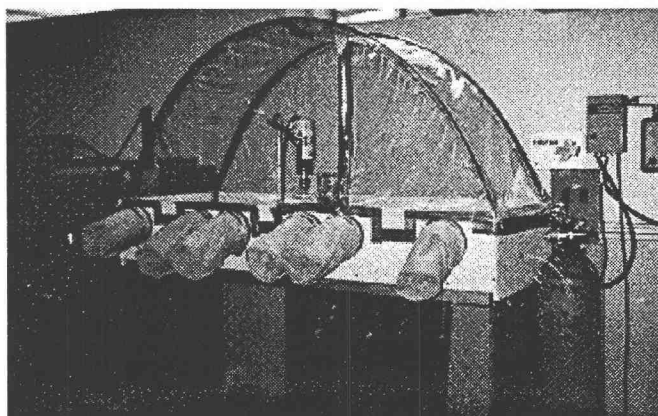


Figure 2b. Glovebox to provide nitrogen ambient to reduce oxidation.

copper sulfate (CuSO_4), disodium ethylenediamine tetraacetate (EDTA), sodium hydroxide (NaOH), and formaldehyde (HCHO). The range over which each component is varied is also reported. The change in the mass of the substrate is measured using a Denver Instruments XE-310 analytical balance. Time is kept using a stopwatch. The temperature of the bath is maintained at either 27°C or 31°C .

The plating experiments are conducted within an inert environment of nitrogen to eliminate the oxidation of the thin copper plated films. The nitrogen hood was

constructed using $\frac{3}{4}$ inch plywood walls with a PVC sheet suspended by two metal hemispheres. Nitrogen is supplied through a bleeder hose which lines the interior of the hood. An oxygen sensor is used to measure the overall oxygen content of the hood environment. The oxygen concentration is always below 4%.

A 3 inch diameter copper disk serves as the substrate for deposition. This disk is fastened to a $3\frac{1}{2}$ inch diameter polyethylene disk by a nylon bolt to ensure flatness and centering. Due to the coverage of a portion of the copper disk by the head of the nylon bolt, the total available area for the plating is 45.18 cm^2 . The copper disk is handled within the nitrogen hood using wafer pincers. Nitrogen is used to drive oxygen from the hood as well as dry the substrate following a rinse so that it could be weighed.

Table 1. Composition of the plating solution used for electroless copper deposition.

Species	Base Case	Range
CuSO_4	0.05 M	0.01 - 0.07 M
EDTA	0.14 M	0.076 - 0.30 M
NaOH	0.30 M	fixed
HCHO	0.50 M	fixed

II.2. Procedure

In this section, the experimental procedure for electroless copper deposition is described. The copper disk is cleaned using a wire wheel in order to remove obvious

detritus. The disk is then scrubbed using a pumice cleaner. After a rinse with water, the disk is subjected to a series of rinses which consist of acetone, methanol, and distilled water. These steps are performed outside of the inert hood so as to minimize any accumulation of volatile vapors within the hood.

The disk is then placed in a container which holds an alkaline solution ($\text{pH} = 10$) to prevent any oxidation of the surface. The container is then placed inside the inert hood.

The plating solution is prepared outside of the hood. The reagents are weighed and added in the following order: formaldehyde first, EDTA second, copper sulfate third, and sodium hydroxide last. It is important to add the EDTA prior to the copper sulfate, as the ligand prevents an immediate plating out of the cupric ions in solution. The plating bath temperature is recorded and the bath is then placed within the inert hood.

The hood is then sealed and compressed nitrogen allowed to enter the chamber until the oxygen percentage of the environment drops to below 4%. The copper disk is then removed from the alkaline solution and rinsed using deionized water. Compressed nitrogen is used to dry the disk, whereupon the disk is weighed using an analytical balance which is accurate to a thousandth of a gram. The copper disk is then secured to the polyethylene disk using a nylon bolt. The disk is mounted on the substrate, and the solution is moved into position and the timer and motor are started.

When the desired time period has elapsed, the disk plating solution is removed from position and the timer and the motor are stopped. The copper disk is then removed from the polyethylene disk and rinsed with deionized water. The copper disk is dried using compressed nitrogen and weighed. The weight is recorded and the copper disk is

then placed back in position on the polyethylene disk, the plating solution moved into position, and the motor and timer started. This procedure is repeated for the duration of the experiment.

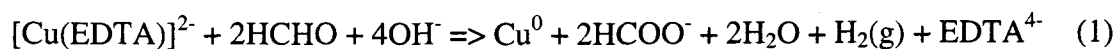
The experimental runs are performed with specific goals in mind. The initial experiments are to establish the repeatability and reproducibility of the process. The objective of the second round of experiments is to determine the rotation speed at which the plating became reaction rate limited. In order to determine the reaction order with respect to the cupric ion concentration, the third round of experiments varies the CuSO_4 concentration while keeping the remaining reagents constant. The ligand concentration is varied so as to discern the effect it has upon the plating rate. Finally, to compare the model prediction of the plating process to the actual observed plating rate, a group of runs is performed varying the cupric ion concentration and the rotation speed. Table 2 shows the experimental conditions employed for each set of runs examined in this study.

Table 2. Experimental conditions for each set of runs examined in this study.

Goal	Bath Composition	Component Varied
Reproducibility (Base Case Bath)	0.05 M CuSO ₄ , 0.14 M EDTA, 0.50 HCHO, 0.30 M NaOH T = 27 °C	none
Kinetics Limited Regime Determination	Base Case Bath T = 31 °C	Rotation Speed (0 - 200 RPM)
Cupric Ion Order Determination	0.14 M EDTA, 0.50 HCHO, 0.30 M NaOH, 200 RPM T = 31 °C	CuSO ₄ (0.01 M - 0.07 M)
Ligand Test	0.05 M CuSO ₄ , 0.50 HCHO, 0.30 M NaOH, 50 RPM T = 31 °C	EDTA (0.076 M - 0.30 M)
Model Test	0.50 HCHO, 0.30 M NaOH T = 31 °C	CuSO ₄ (0.01 M - 0.07 M) Rotation Speed (20 - 200 RPM)

III. MODEL

The overall reaction expression for electroless copper deposition can be written as follows:

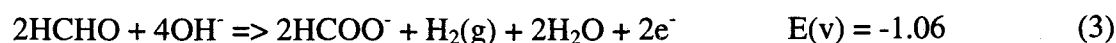


The cupric ions are reduced by the formaldehyde in a caustic environment to form the copper metal film. The plating is believed to proceed through the following oxidation-reduction couple [Shachem-Diamand, 1995]:

Cathodic Reduction:



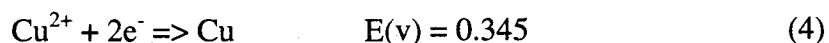
Anodic Oxidation:



The reported anodic potential is for a pH of 11.5 and a hydrogen partial pressure of 1 atm. To prevent the reduction of the cupric ions in solution, a chelating ligand (EDTA) is added to the bath to ensure the deposition of the copper upon the substrate. This complexing reaction is assumed to be fast enough that it does not significantly affect the overall plating rate. This assumption is validated by the fact that the copper would otherwise plate out in solution if the cupric ions were not significantly complexed.

In order for plating to occur, the redox potential of the oxidation reaction must be more negative than the reduction reaction. Inspection of reaction (3) indicates that an alkaline environment is a necessary condition for the reduction of the cupric ions.

However, the difference in the redox potentials of the reducing and oxidizing reactions should not be too large, or the metal will tend to plate out in solution. Chelating ligands may reduce the difference in potentials by decreasing the metal redox potential through complex formation [Shachem-Diamand, 1995]. The redox potential of the uncomplexed cupric ion is:



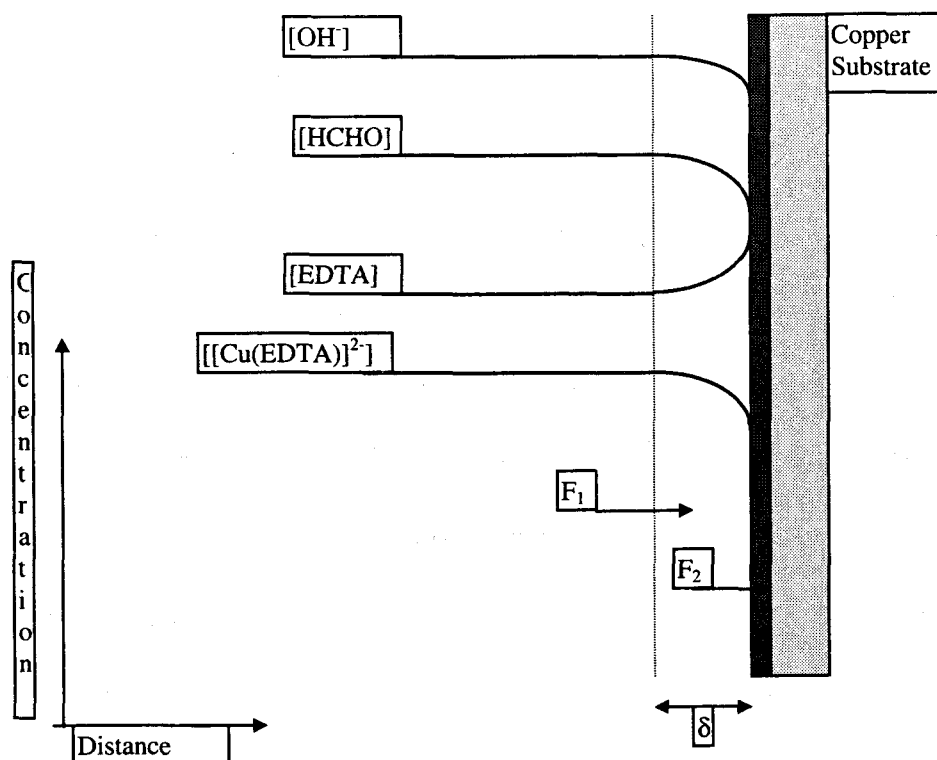
The addition of the EDTA lowers the absolute redox potential difference by approximately 0.561 volts. Other complexing agents will result in different thermodynamics.

The actual rate of copper plating upon the substrate depends on many processes. The mass transfer of the cupric ion complex to the board, the absorption of the copper complex, its orientation and surface diffusivity, the reduction of the cupric ions and oxidation of formaldehyde, and the transport of the reactants away from the substrate surface all enter into play. In this study, it is assumed that there are two significant processes: the mass transfer of the cupric ion complex from the bulk of the plating solution to the surface of the substrate and the reaction of the cupric ion complex at the substrate surface which results in the formation of the copper film. At steady state, the fluxes from these processes are equal.

The plating bath used in this work is comprised of copper sulfate, sodium hydroxide, formaldehyde, and EDTA in deionized water. The copper sulfate is kept as the limiting reagent, with all other reactants present in stoichiometric excess. Figure 3 shows a schematic of the concentration profiles of these species in the plating bath. The concentration profiles are constant in the bulk solution. Within the boundary layer (of

thickness, δ), on the other hand, the concentration of all species changes with distance.

The flux of cupric ion-EDTA complex is denoted F_1 while the flux due to the surface reaction is denoted F_2 .



F_1 = flux of cupric ions due to mass transport (moles/cm²*s)

F_2 = flux of cupric ions due to reduction reaction (moles/cm²*s)

δ = boundary layer thickness (cm)

$[\]$ = concentration of reactant (moles/cm³)

Figure 3. Model of electroless copper deposition.

The flux due to mass transfer can be represented mathematically as:

$$\text{Mass Transport} = F_1 = h_g ([Cu(EDTA)^{2-}]_{bulk} - [Cu(EDTA)^{2-}]_s) \quad (5)$$

where h_g is the mass transfer coefficient (cm/s). The subscripts, bulk and s, refer to the bulk solution and substrate surface, respectively. The flux due to the reduction of the cupric ions is represented as:

$$\text{Reaction} = F_2 = k_s [OH^-]_{bulk}^b [HCHO]_{bulk}^c [Cu(EDTA)^{2-}]_s^a \quad (6)$$

where k_s is the reaction rate constant for copper deposition. The reaction orders with respect to hydroxyl ion, formaldehyde, and cupric ion complex are b, c, and a, respectively. Due to the fact that the cupric ions are maintained as the limiting reactant and the hydroxyl and formaldehyde concentrations are in stoichiometric excess throughout the experiments, the rate law uses the bulk concentrations of the hydroxide ion and formaldehyde and the surface concentration of the cupric ions.

In order to quantify the mass transfer of the cupric ion complex, a rotating copper disk is used as the substrate. In this manner, the surface concentration of the cupric ion complexes may be quantified. The rotation of the disk pulls reactants to the disk surface and spins the fluid volume along with it. Figure 4 illustrates the streamlines and the velocity components of the rotating disk.

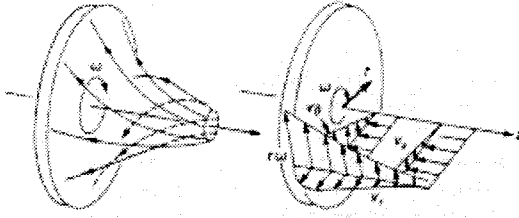


Figure 4. Streamlines and velocity components of the rotating disk (taken from [White, 1974]).

The mass transfer of the cupric ion complex to the substrate surface is diffusion limited within this boundary layer. The diffusion boundary layer thickness is a function of the disk rotational speed, solution kinematic viscosity, and the diffusion coefficient of the cupric ion complex. The mass transfer coefficient for a rotating disk is given by [Cussler, 1984]:

$$h_g = 0.62 \frac{D}{d} (w \frac{d^2}{\nu})^{1/2} (\frac{\nu}{D})^{1/3} \quad (7)$$

where

d = disk diameter (cm)

w = rotational speed (rad/s)

ν = kinematic viscosity of fluid (cm²/s)

D = diffusion coefficient of relevant species (cm²/s)

This expression is valid up to a Reynolds number of 2.5×10^5 , where

$$Re = wd^2/\nu \quad [\text{Lal, 1980}]$$

The diffusion coefficient for the cupric ion complex and the kinematic viscosity of the bath are determined using the correlations developed by Ying [Ying, 1988] and give a diffusion coefficient of 4.44×10^{-6} cm²/s and a kinematic viscosity of 0.0099 cm²/s at 31

°C for the base case conditions. This work assumes that the chelating ligand concentration does not affect the plating rate directly. Rather, a minimum amount of ligand is required to prevent cupric ion from being reduced in solution, but an excess will not significantly alter the overall plating rate. The main effect of the ligand is the complexing of the cupric ions, and as such, the diffusion coefficient of the complex is used to determine the mass transfer of the cupric ions to the substrate. It should be noted, however, that different chelating ligands will have different effects upon the redox potential of the cupric ion reduction reaction, and will therefore result in different inherent reaction kinetics.

At steady state, the fluxes are equal:

$$F_1 = F_2 = h_g ([Cu(EDTA)^{2-}]_{bulk} - [Cu(EDTA)^{2-}]_s) = k'[Cu(EDTA)^{2-}]_s^a \quad (8)$$

With the substitution:

$$k' = k_s [OH^-]_{bulk}^b [HCHO]_{bulk}^c \quad (9)$$

Thus by measuring the flux of copper to the board one may quantify the unknown parameter $[Cu(EDTA)^{2-}]_s$. The reaction order a , and the reaction rate constant k' may then be found by varying the concentration of cupric ions initially in solution and measuring the plating rate.

IV. RESULTS AND DISCUSSION

IV.1. Reproducibility

There are two sets of runs performed to ensure reproducibility of the data obtained from the experimental runs. The first set involves three runs at four hours apiece using the base case bath concentrations at 27 °C at 50 RPM. Table 3 shows the mass of copper plated for these three runs. These values are within 6% of one another. The reported uncertainty of ± 1 milligram results from the error associated with the analytical balance.

Table 3. Mass of copper plated under identical experimental conditions.

Bath #	Mass of Plated Copper (milligrams)
1	61 ± 1
2	59 ± 1
3	63 ± 1

Figure 5 shows continuous and stepwise mass measurements for the deposition conditions reported above. Continuous measurements refer to the procedure whereby the copper disk is removed from solution and weighed and then the same disk is placed back into solution and the reaction allowed to continue. In the stepwise readings a new solution

is made up and a clean disk inserted for each time measurement. Clearly, continuous measurements are a more efficient method of data collection.

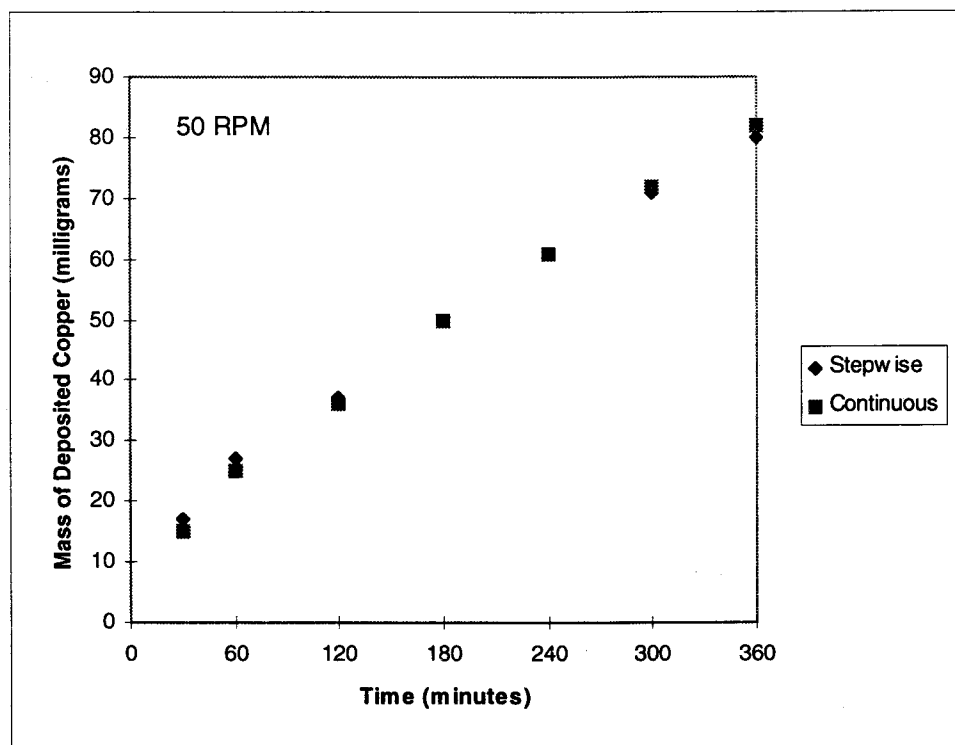


Figure 5. Comparison of continuous versus stepwise measurements at base case bath conditions at 50 RPM. See text for definitions of continuous and stepwise.

Figure 6 depicts the deposition rate versus time for the data in Figure 5. The plating rates are obtained from the difference in the mass between successive data points and reported for time halfway between measurements. A copper film density of 8.93 g/cm^3 is used. For example, the mass difference between 1 hour and 2 hours is divided by 1 hour and converted to $\mu\text{m/hr}$ using the copper film density to obtain the rate of deposition and the value is reported at 1.5 hours. Within the experimental uncertainty,

the continuous and stepwise methods of data collection are equivalent. Thus in this work, all reported data are collected via the continuous method.

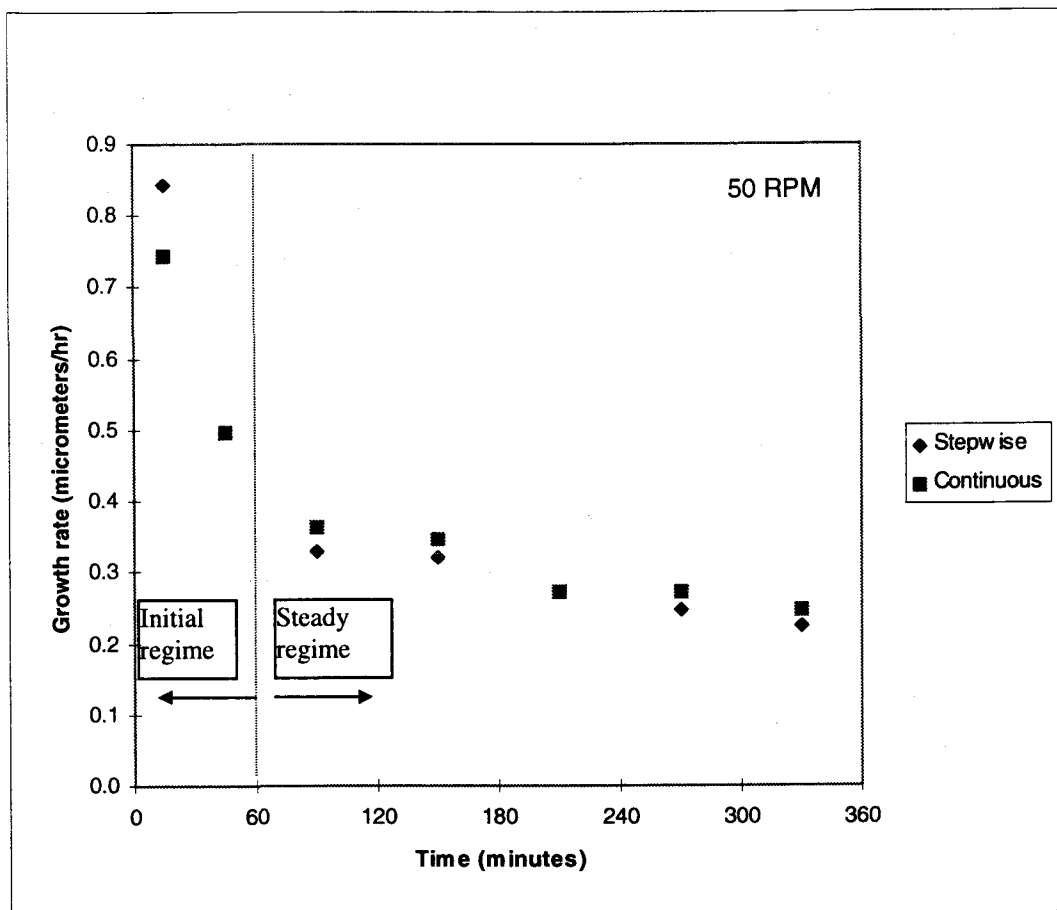


Figure 6. Growth rate versus time for the stepwise and continuous runs using the base case bath at 50 RPM.

In these data sets, there are two regimes of copper growth: an initial regime where the growth rate is relatively fast but falls off quickly and a steady regime where the growth rate is slower but only tapers off gradually. These regimes are labeled in Figure 6. The steady regime seems to occur after one hour of plating. The different regimes of electroless copper deposition will be discussed in more detail in section IV.2.

IV.2. Rotation Speed Variation

Figure 7 shows the mass of deposited copper versus time for a series of runs where the rotational speed of the copper substrate is varied. Again the compositions of solution constituents are kept at the base case values. Figure 8 presents the incremental plating rate versus time, which is calculated as discussed earlier.

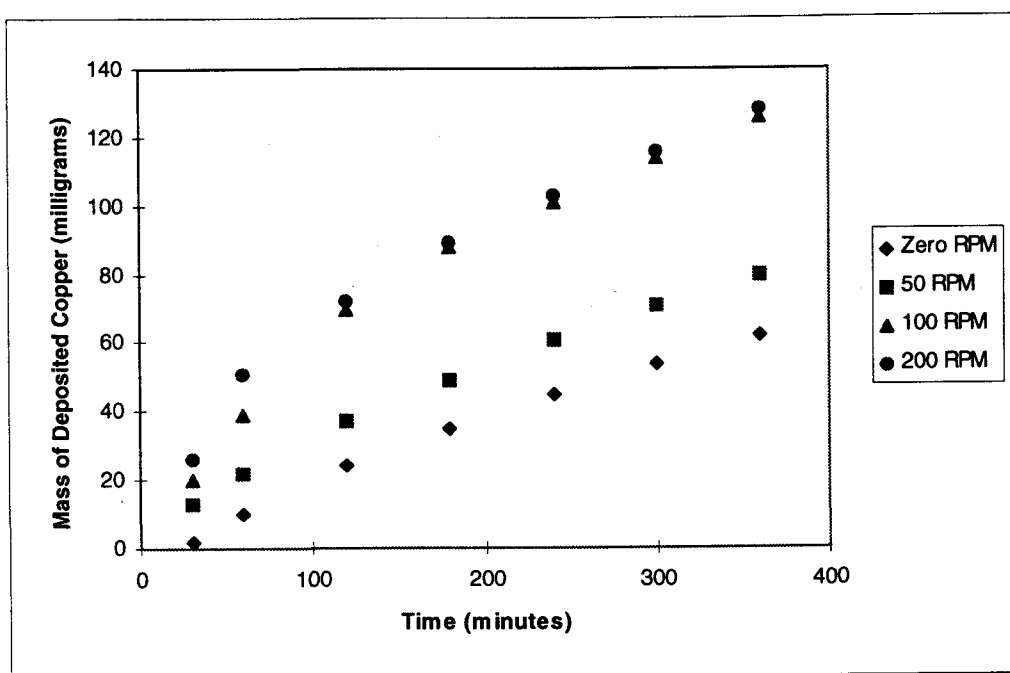


Figure 7. Mass of deposited copper versus time for the base case bath over a range of rotation speeds.

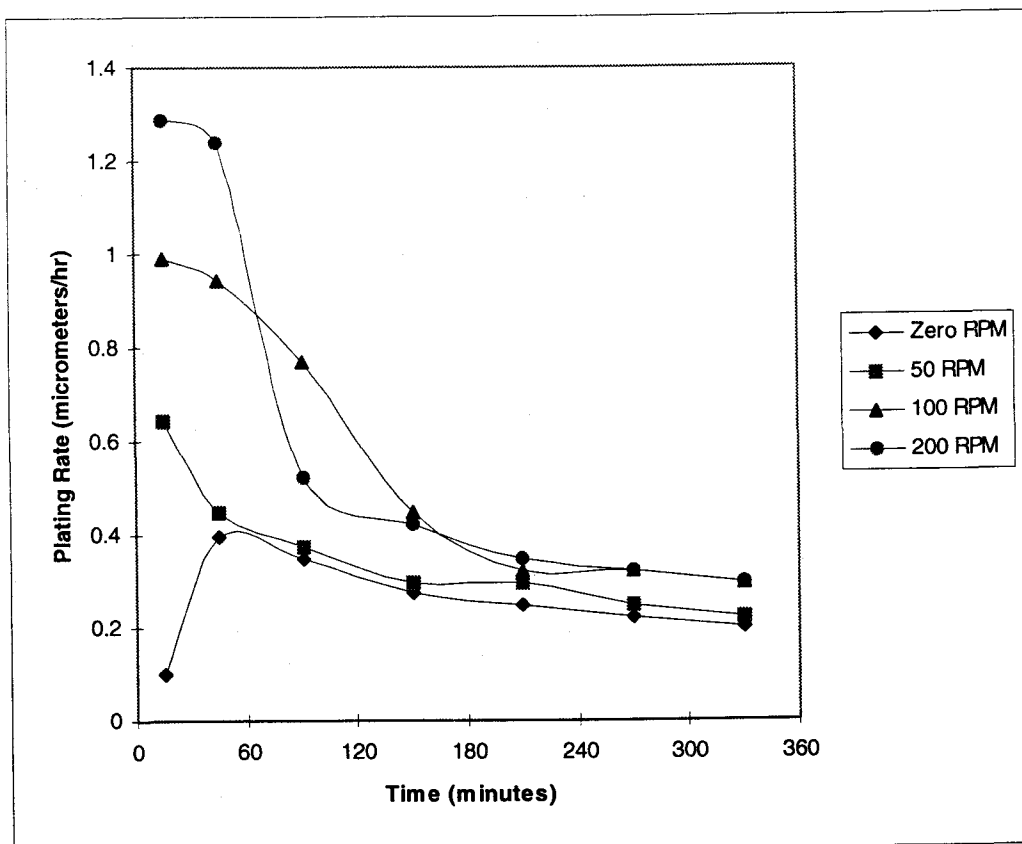


Figure 8. Plating rate versus time using the base case bath concentrations at varying rotation speeds.

Figure 8 manifests the two regimes of growth discussed previously. The duration of the initial regime depends upon rotation speed. For example, at 200 RPM the plating rate drops precipitously between 45 and 90 minutes, indicating a change in the growth regime. However, at 100 RPM the steady growth regime is only reached at 150 minutes. Thus the growth rate at 100 RPM is greater than that at 200 RPM after 90 minutes. Once the steady regime has been established, the growth rates for 100 RPM and 200 RPM coincide. A third growth regime is noticed for a zero RPM rotational speed. In this case, the growth rate initially increases with time unlike the other three data sets. This regime is labeled the nucleation regime and will be discussed shortly.

The mass transfer coefficient increases with increasing rotational speed since the boundary layer thickness decreases. Table 4 reports the calculated mass transfer coefficient, h_g , as a function of the rotation speed of the substrate. These values are calculated according to equation (7), using a value of $4.44 \times 10^{-6} \text{ cm}^2/\text{s}$ for the diffusion coefficient and a value of $0.0099 \text{ cm}^2/\text{s}$ for the kinematic viscosity. Table 4 also reports the growth rate at 15 minutes, R_{15} , and the ratio of R_{15}/h_g .

Table 4. Variation of the mass transfer coefficient, h_g , with rotation speed.

Rotation Speed (RPM)	$h_g \times 10^3 \text{ (cm/s)}$	$R_{15} \text{ (}\mu\text{m/hr)}$	$R_{15}/(h_g \times 10^3)$
50	0.83	0.64	0.77
100	1.17	0.99	0.85
200	1.66	1.29	0.78

If growth is mass transport limited, the surface concentration of the copper ion-EDTA complex goes to zero. In this case, the growth rate will be proportional to the mass transfer coefficient for the same bulk copper ion-EDTA concentration, as inspection of equation (5) shows. Table 4 indicates that this condition is met in the initial growth regime i.e. after 15 minutes of growth. Hence, for the large growth rates which occur initially, the electroless deposition of copper is mass transfer limited.

When the plating rate is independent of the rotation speed, the reaction rate is much slower than the mass transfer rate. A sufficient amount of cupric ions are transporting to the substrate and the reduction reaction is completely surface reaction rate

limited. At this point, the reaction is the slow step and the plating flux is controlled by the reduction of the cupric ion complex at the substrate surface. In the steady regime, the identical plating rates for rotational speeds of 200 RPM and 100 RPM indicate at this point the overall plating process is surface reaction limited.

At rotational speeds of 100 and 200 RPM, the shift from the initial to the steady regime seems to occur after 40 milligrams of electroless copper are deposited upon the copper disk, which corresponds to a copper film approximately 1 μm in thickness. In previous studies the steady plating rate occur after a film thickness of only 0.033 μm is deposited [Dumesic, 1974]. The differences in the amount of electroless copper at which the rate changes may be ascribed to the differing substrate conditions. In the study by Dumesic, a palladium activated glass substrate is employed, whereas this study used a copper surface. Dumesic found that the initial plating rate is affected by the amount of palladium catalyst used to activate the substrate surface. Heavier activation produces faster initial rates, however, the final rate in his study remains independent of the activation conditions.

A possible explanation for the faster deposition rate exhibited by the initial portion of the plating process is that the surface of the copper substrate becomes smoother with time as the plating proceeds. It is observed that the electroless copper bath will cause plating to occur upon ridges and nicks in the glass reactor vessel, thus these rough spots provide nucleation sites for growth. This phenomena may occur on the atomic level as well, with the cupric ions thermodynamically favoring steps to deposit upon. As the film grows, the topography becomes smoother [Radoeva, 1995], thus slowing down the surface migration step in the plating process. Also, the rougher surface provides more

overall surface area for the copper to deposit upon. As the substrate smoothes out with time, this available area decreases.

The analysis of the rate law in this study uses data obtained after the film growth is in the steady regime. The final plating rates obtained are approximately 5-10 times slower than those obtained using a catalyzed surface with comparable bath conditions. This phenomena is noticed by others who have used a non-activated copper substrate [El-Raghy, 1979]. This suggests that some property of the catalyzed surface comes into play even at longer plating times, which is contrary to the conclusion reached by Dumesic. Dumesic did not use a completely non-activated substrate in his study, therefore there is some effect caused by the palladium catalyst sites which are initially present upon the plating substrate even after the film has completely covered the catalyst. This may be caused by the change in catalytic activity of the electroless copper film when the palladium is embedded within it. It is known that differing metal substrates exhibit different electrocatalytic properties [Bockris, 1972]. Thus there would appear to be some contribution that the palladium sites offer which is able to alter the plating rate of the electroless copper film in the steady regime. It is also possible that the palladium preferentially segregates to the surface during growth.

It is observed that in the steady regime the plating rate is not actually constant as the reaction proceeds. This may be due to several factors. One is that the copper in solution is being depleted and thus the surface concentration of the cupric ions is lessened. The runs are performed such that less than 5% of the initial bulk cupric ions are consumed; however, this may be an insufficient limitation to provide a constant deposition rate. The inherent kinetics of the plating reaction may change as the reactants

are consumed. The redox potential difference decreases as the pH goes down when hydroxyl anions are consumed by reaction (3). This may affect the nature of the redox couple to the point where the reaction will taper off with increasing time. It was noted that for runs using base case bath conditions with a rotational speed of 200 RPM, the pH decreases by as much as 6%. Another consideration is that the surface morphology of the copper substrate changes as plating goes on. This may affect the adhesion and/or the catalytic properties of the plating surface. The same tapering of the flux with time is seen for both this work and that reported by Mishra using a palladium catalyzed surface [Mishra, 1996]. This implies that the tapering of the flux with time may be independent of the palladium catalyst; rather, it is an inherent consequence of the electroless copper plating process.

At zero RPM a third regime occurs early in the film growth where the growth rate is quite slow. We suggest the retarded growth rate may be due to insufficient nucleation sites upon the substrate. Since the substrate is not rotating, less copper ion-EDTA complex is available to promote nucleation. Moreover, the agitation from the rotation may add to this effect. Thus, growth is slow until enough nucleation sites are established.

IV.3. Cupric Ion Bulk Concentration Variation

Figure 9 shows the plating rate versus time for a series of runs where the initial cupric ion concentrations present in the plating bath is varied with the remaining constituents kept constant at base case bath conditions. A rotation speed of 200 RPM is

used to enhance the mass transfer rate. At this rotation speed, deposition in the steady regime is limited by the intrinsic kinetics of the surface reaction.

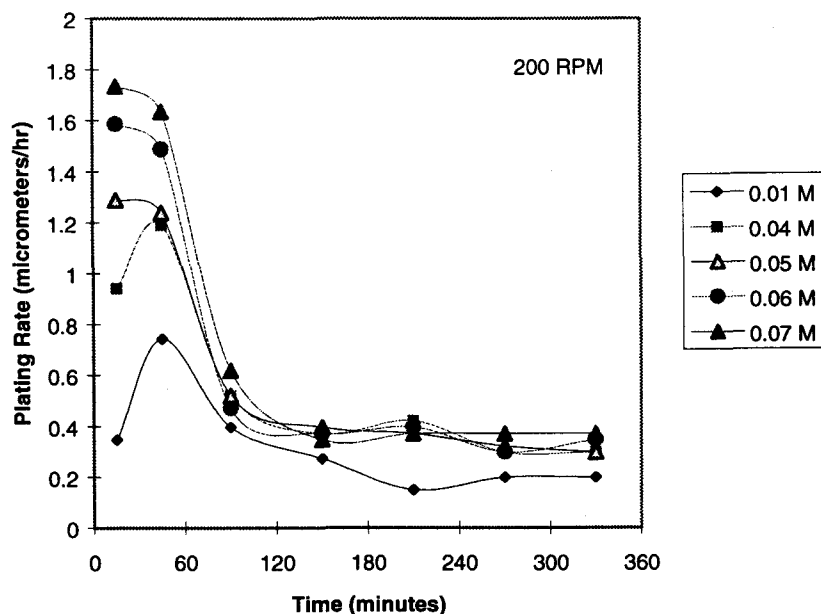


Figure 9. Plating rate versus time for the base case bath at 200 RPM over a range of initial bulk cupric ion concentrations.

Figure 9 exhibits the three regimes of electroless copper deposition. The shift from initial to steady regime occurs after approximately 90 minutes. For cupric ion concentrations of 0.01 M and 0.04 M the nucleation regime is also present, where the insufficient nucleation of the substrate may lead to a growth rate which begins slowly then speeds up once a sufficient amount of sites are present. The growth is then able to enter the initial regime, and finally tapers off once the steady regime is achieved.

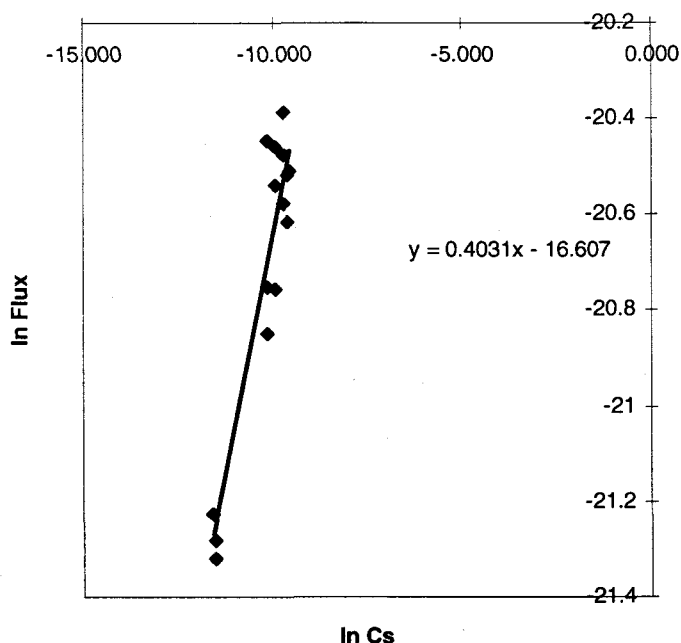


Figure 10. Logarithm of the flux, F_2 , versus the logarithm of the surface concentration of the cupric ion complex for order determination.

Inspection of equation (8) shows that the order of reaction with respect to the cupric ion-EDTA complex surface concentration may be calculated as a proportionality between the logarithm of the flux, F_2 , and the cupric ion complex surface concentration. A plot of the logarithm of the cupric ion flux versus the cupric ion surface concentration is shown in Figure 10. A best fit line is included in Figure 10 and the slope obtained is reported as the order of the reaction with respect to the cupric ion surface concentration. The cupric ion complex surface concentration was determined using equation (5), with F_1 calculated from the recorded mass of plated copper versus time data. The points included

for analysis are all taken after 3 hours of plating to ensure the steady electroless copper growth regime has been reached.

The slope of the line is equal to the reaction order with respect to the cupric ion-EDTA complex concentration. The calculated value of 0.40 is consistent with those reported in the literature [Donahue, 1980]. The scatter in the data may be attributed to the tapering of the plating flux with time. Table 5 shows the calculated order with respect to the cupric ion concentration at three distinct times in the steady regime.

Table 5. Cupric ion order over time.

Time (hours)	Cupric Ion Order
3.5	.413
4.5	.397
5.5	.406

IV.4. Ligand Effects

Figure 11 shows the mass of deposited copper versus time for four EDTA ligand concentrations. These runs are conducted using base case compositions of the other chemical species and at a rotation speed of 50 RPM. A lower rotational speed is used since ligand concentration can potentially effect the mass transfer rate, as well as the intrinsic kinetics.

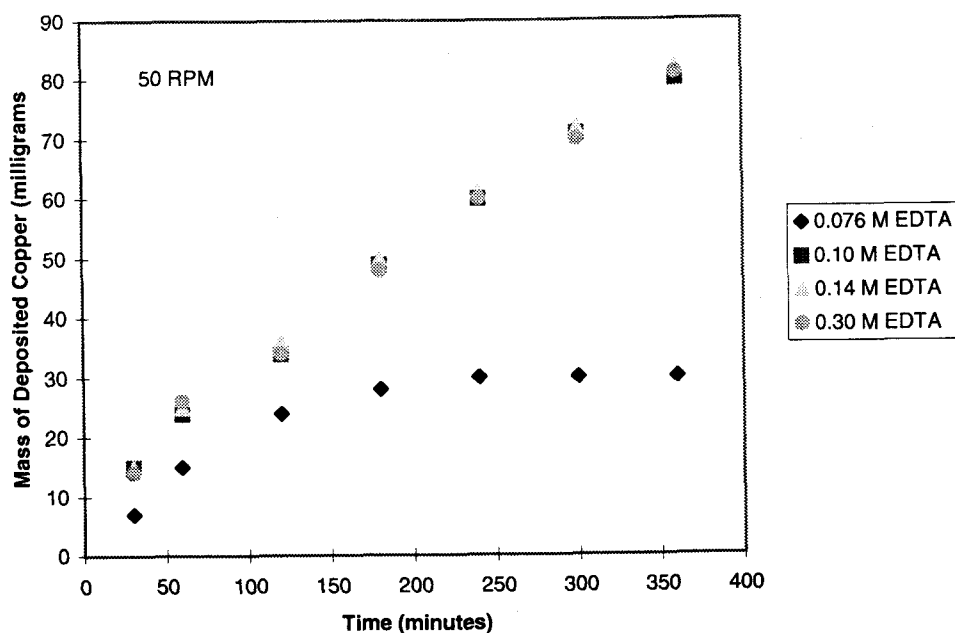


Figure 11. Mass of deposited copper versus time using the base case bath at 50 RPM with varying EDTA concentration.

The runs for EDTA concentrations of 0.10 M, 0.14 M, and 0.30 M yield almost identical deposition of copper with time. The run performed with 0.076 M EDTA produces a lower deposition than those above. It is observed that during the 0.076 M EDTA run the cupric ions plates out in solution, thus impeding the plating of the copper upon the rotating copper disk. Increasing the EDTA concentration allowed the copper to complex in solution such that the copper that plated out is confined to the rotating copper substrate. Thus it would seem that the EDTA concentration has little to do with the rate of copper deposition other than a minimum amount of chelating ligand is necessary to keep the cupric ions from being reduced in solution. It is for this reason that the ratio of EDTA to cupric ion concentration is kept in excess of 2 for the experimental runs.

IV.5. Calculation of Rate Law

The data obtained in determining the flux of the cupric ions at 200 RPM with varying initial cupric ion bulk concentration are used to determine the plating rate of the copper film within the steady regime. The values for the flux are calculated using data taken after the third hour of plating in order to ensure the steady regime has been reached. Table 6 shows the value of k' versus cupric ion concentration. The value of k' obtained is $6.75 \pm 0.16 \cdot 10^{-8}$ cm/s.

Table 6. Calculated value of k' for each run at a rotational speed of 200 RPM.

Cupric Ion Concentration (moles/L)	$10^8 \cdot k'$ (cm/s)
.01	6.67
.04	6.95
.05	6.86
.06	6.53
.07	6.73

Thus in the steady regime, the flux is determined to be:

$$F_2 = (6.75 \pm 0.16) \cdot 10^{-8} [Cu(EDTA)^{2-}]_s^{0.40 \pm 0.01} \quad (\text{moles/cm}^2 \cdot \text{s}) \quad (10)$$

If a film density of 8.93 g/cm^3 is assumed, then the growth rate, R , may be expressed as:

$$R = (17.28 \pm 0.41) [Cu(EDTA)^{2-}]_s^{0.40 \pm 0.01} \quad (\mu\text{m/hr}) \quad (11)$$

The reported error of the reaction order and the reaction rate constant are determined by taking the standard deviation values in Tables 5 and 6, as well as accounting for the uncertainty associated with the mass measurements.

IV.6. Model Comparison

Table 7 shows the predicted and measured growth rates for the differing experimental conditions. The ratio of the surface concentration to the bulk concentration of the cupric ion complex is shown, as well as the error between the model prediction and the measured growth rates. The surface concentration of the cupric ion complex is determined using equations (7) and (8) with a k' value of 6.75×10^{-8} . The error is calculated by dividing the absolute value of the difference of the predicted and measured values by the measured value and multiplying this result by 100%.

The ratio between the surface concentration and the bulk concentration of the cupric ion complex is always above 0.89, suggesting that the effects of mass transfer in the steady regime is limited. The slow intrinsic kinetics dominate the growth in the steady regime. The model predicts the measured data to within 13%. It should once again be noted that the plating rate obtained is for the steady regime only.

Table 7. Model predictions as compared to the measured growth rates.

[CuSO ₄] (moles/L)	Rotation Speed (RPM)	$[\text{Cu}^{2+}]_s$	Predicted Growth (P) ($\mu\text{m/hr}$)	Measured Growth (M) ($\mu\text{m/hr}$)	Error 100%* (P-M)/M (%)
		$[\text{Cu}^{2+}]_{\text{bulk}}$			
0.05	100	0.971	0.325	0.314	3.5
0.05	80	0.967	0.324	0.316	2.5
0.05	20	0.936	0.321	0.285	12.4
0.01	50	0.890	0.164	0.174	5.0
0.03	50	0.944	0.262	0.285	8.1
0.04	50	0.953	0.295	0.291	1.3
0.05	50	0.959	0.323	0.304	6.5
0.07	50	0.967	0.372	0.353	5.1

V. CONCLUSIONS AND RECOMMENDATIONS

V.1. Conclusions

The work in this thesis is performed in an attempt to gain a better understanding of the processes which govern the electroless copper plating rate. In order to do this, a fundamental chemical engineering analysis is applied to the system which decoupled mass transport from intrinsic reaction kinetics. The results of this work are summarized as follows:

- Three plating rate regimes are found to exist in this study: an initial regime which is mass transfer limited, a steady regime which is surface reaction limited, and a nucleation regime where growth is believed to be limited by the number of available sites.
- The reaction rate for the steady regime with copper as the limiting reagent and the formaldehyde and sodium hydroxide concentrations held at 0.50 M and 0.30 M, respectively, is found to be:

$$R = (17.28 \pm 0.41)[\text{Cu(EDTA)}^{2-}]_s^{0.40 \pm 0.01} \quad \mu\text{m/hr}$$

- The plating rate is found to be independent of the EDTA concentration above an atomic ratio of EDTA to CuSO_4 of 2:1.
- The proposed model predicts the plating rates to within 13% of the measured values.

V.2. Recommendations

The following recommendations are suggested for future work:

- The disk geometry could be replaced by a ring which is embedded within the polyethylene disk.
- A catalyzed substrate should be employed to quantify the differences between the bare copper surface and an activated surface and increase the intrinsic reaction rate in the steady regime.
- Order determination for the remaining reactants, hydroxide and formaldehyde, should be done to complete the rate law expression.
- Potential measurements with time should be added to the experimental procedure.
- Temperature effects upon the rate should be examined.
- Surface analysis techniques such as scanning electron microscopy and atomic force microscopy should be used to examine the topography of the copper substrate in each of the growth regimes.

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